POLAROGRAPHIC REDUCTION OF COBALTIC COORDINATION COMPOUNDS

BY

HENRY FULLER HOLTZCLAW, JR.

A. B., University of Kansas, 1942

M. S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The primary difficulty in polarographic study of cobaltic coordination compounds, heretofore, has been a lack of knowledge as to the proper conditions under which to work. Herda[1] ran a series of over thirty coordination compounds on the polarograph, using gelatin as a maximum suppressor and a minute droplet of octyl alcohol to prevent foaming of the gelatin solution. Willis, Friend, and Mellor[2] ran polarographic reductions on a number of cobaltic compounds, including one of the series run by Herda, in sulfate medium without the use of maximum suppressing agents. The general trends of the work of Herda and that of Willis and coworkers are in agreement, but the absolute values are not.

Quagliano[3] showed that both gelatin and octyl alcohol in the amounts used by Herda change the half-wave potentials. The general trends of Herda's work seem to be accurate, but the absolute values, therefore, are true only under the special conditions used. Quagliano found that the half-wave potentials are less negative in solutions of the indifferent electrolytes which have little or no tendency to coordinate, such as nitrate and perchlorate, than in those which do possess marked coordinating powers. The present work confirms and expands these findings, showing that values given by Willis, Friend, and Mellor were affected by the use of sulfate as a medium.

It was desired, in the present investigation, to extend the work of Quagliano by studying half-wave potentials, diffusion currents, and slopes of curves for both reduction waves and to try indifferent electrolytes, possessing varying coordination abilities, in various concentrations. In connection with these measurements, studies were made of the relation-

ship of diffusion current to drop-time in order to determine a drop-time for which the Ilkovic equation would come nearest to being valid.

Another section of the present investigation was devoted to postulation of a possible method of differentiation of cis and trans isomers for certain types of cobaltic coordination compounds. The ion containing the cobalt possesses a permanent dipole in addition to an electrical charge if the dissimilar coordinated groups are unsymmetrically arranged around the cobalt ion. This situation pertains to the cis isomer of a compound containing two charge types of coordinated groups but not to the trans isomer with its symmetrical grouping. Thus, the cis isomer should orient with respect to the dropping mercury electrode and undergo movement toward the electrode because of the non-homogeneous electric field around the electrode and the resulting greater attraction of the electrode for the cis isomer than for the trans. The migration current, therefore, should be greater for the cis isomer than for the trans. The reduction would necessarily have to take place in the absence of indifferent salts so that the migration current would constitute a measurable amount of the total current.

Experimental

A Sargent Polarograph Model XX, which is equipped with a Brown Strip Chart Recorder, was used in this investigation. Dissolved oxygen was removed from the electrolysis cell by passage of purified nitrogen through the cell prior to each run. The anode for the cell was a quiet mercury pool; the cathode, a dropping mercury electrode. The measurements of potential in indifferent electrolyte media were made against an external saturated calomel electrode. The calomel electrode was not used in the portion of the problem dealing with cis and trans isomers because of the danger of introducing foreign salts into the solution and because half-wave potential measurements were not necessary for that

phase of the work. A student-type potentiometer, with accessories, was connected into the circuit so that measurements of potential would be more accurate than those given by the polarograph. The complex salts used were prepared by methods given in the literature.

Discussion

A study of the polarographic reduction of hexamminecobaltic ion was made using various indifferent electrolyte solutions as media. The results indicated more negative half-wave potentials and lower diffusion currents approximately in the order of increase of the coordinating power of the negative ions of the indifferent electrolytes used. For indifferent electrolytes having significant coordinating ability, the half-wave potentials became more negative and the diffusion currents became lower with increasing concentration of the indifferent electrolyte. These results led to the postulation of a "super-complex" in which the original cobalt complex acts as the center of the super-complex. Ions of the indifferent electrolyte are thought to be clustered about the central complex by an electrostatic attraction in a manner similar to that expressed by the ion-pair concept of Bjerrum[4,5] and of Kraus[6,7].

The slopes of the curves indicated irreversible behavior in all cases, but less irreversible with some indifferent electrolytes than with others. The results of this work indicated that the reduction to the cobaltous state is accompanied by a *simultaneous* aquation of the cobaltous ion.

In the study of the cis and trans isomers, experimental data for cis and trans dinitrotetramminecobaltic ions, in the absence of indifferent electrolytes, substantiated the predicted trend. Most favorable results with regard to maximum suppression and stability of the solutions appeared in twenty-five per cent ethyl alcohol solutions of the salt. Predictions were made of the migration currents for cis and trans isomers for positive ions in which the coordinating groups are all

neutral and for negative ions. Satisfactory ions for use in verifying the predictions for these two cases were not found.

SUMMARY

1. Experiments were run to establish optimum drop-time for most favorable conformity to the Ilkovic equation.

2. Determination of half-wave potentials and diffusion currents for hexamminecobaltic chloride in various indifferent media of varying coordinating abilities and varying concentrations led to the postulation of a "super-complex" in which anions of the indifferent electrolyte are thought to be clustered about the central complex by an electrostatic and ion-dipole attraction.

3. Determination of the slopes of the curves in the various indifferent media indicated irreversible reduction, thought to be due to a simultaneous aquation of the cobaltous complex during the reduction of the cobaltic complex.

4. A method of distinguishing between cis and trans isomers of certain types of cobaltic complex ions was postulated. The theory was verified experimentally for cis and trans dinitrotetramminecobaltic chloride.

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VITA

The author was born on July 30, 1921, in Stillwater, Oklahoma. He attended the public schools of Lawrence, Kansas, graduating from the Liberty Memorial High School of Lawrence in 1938. In June, 1938, he entered the University of Kansas, from which he received the degree of Bachelor of Arts in June, 1942. During the summers of 1941 and 1942, he worked for the Eastman Kodak Company, Rochester, New York. From September, 1942, to September, 1943, he was enrolled in the graduate school of the University of Kansas and held teaching assistantships in chemistry and mathematics. In October, 1943, he entered the graduate school of the University of Illinois and held a teaching assistantship in the Inorganic Division of the Department of Chemistry. From April, 1944, to November, 1945, he worked in Oak Ridge, Tennessee, for the Clinton Engineer Works—Tennessee Eastman Corporation, in the capacity of Shift Foreman of an analytical chemistry laboratory. In November, 1945, he returned to graduate study at the University of Illinois. He held a teaching assistantship in the Inorganic Division of the Department of Chemistry until September, 1946, at which time he was appointed to a University Fellowship which he has held until the present time. He received the degree of Master of Science in Chemistry from the University of Illinois in June, 1946.

The author is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, Pi Mu Epsilon, Alpha Kappa Psi, and Alpha Chi Sigma.

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